

CHARACTERIZATION AND UPGRADING OF COAL LIQUIDS
DERIVED FROM MILD GASIFICATION PROCESSES

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ABSTRACT

Mild gasification processes produce coal liquids that have the potential to be upgraded for use as transportation fuels. The quality and yield of these liquids vary widely depending upon the severity of the gasification process. Chemical upgrading of coal liquids may offer a viable and potentially economical alternative to conventional hydrotreating processes. Coal liquids from the United Coal Company Research Corporation, the KILnGAS, the SGI International, and Coalite (United Kingdom) processes have been characterized. These liquids and some of their distillates were subjected to solvent extraction upgrading with formic, acetic, and phosphoric acids to remove the basic nitrogenous fraction. Nitrogen removal ranged from about 50 to as high as 98%, with a recovery factor of about 75%. The most cost-effective reagent appears to be 25 vol % phosphoric acid.

INTRODUCTION

Mild gasification of coal has been shown to be capable of producing relatively light liquids, possibly suitable as an engine fuel, and char that may be suitable for boiler fuel or other purposes. Process conditions greatly influence the product quality; in particular, liquid product quality suffers with increasing yield (Graves et al., 1984). Some liquid upgrading (or blending) will be required even under mild gasification conditions before these liquids can be successfully utilized as transportation fuels. However, the severity and cost of upgrading are predicted to be less compared with conventional hydrotreating. The economics of upgrading mild gasification liquids varies with the raw liquid quality (Graves and Fox, 1984).

Complete and consistent data for mild gasification liquids are sparse in the literature. Often times, the data are of limited use since they have not been obtained by standard methods. Complete chemical and physical analyses of the liquids are essential to (1) determine the feasibility and degree of upgrading needed to produce marketable products from these liquids, (2) evaluate

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the performance of these liquids as transportation fuels, and (3) optimize the mild gasification processes with respect to product yield and product quality.

In this paper, recent results pertaining to the characterization and chemical upgrading of coal liquids from typical mild gasification processes are presented. The studies were conducted at the Oak Ridge National Laboratory (ORNL) for the Morgantown Energy Technology Center (METC), Department of Energy (DOE). The liquid characterization and upgrading are being conducted in conjunction with the char characterization.

LIQUID CHARACTERIZATION

Coal liquid samples from four mild gasification processes were examined in this study. The liquids examined came from the United Coal Company Research Corporation's mild gasification process development unit (UCCRC MGU) in Bristol, Virginia; from the KILnGAS commercial module being operated by the Allis-Chalmers Coal Gas Corporation in East Alton, Illinois; from the low-temperature pyrolysis process being tested by SGI International at the Salem Furnace Company in Pittsburgh, Pennsylvania; and from the Coalite low-temperature carbonization commercial plant in the United Kingdom. The latter product was supplied by UCCRC. Information on the processes is limited since it is deemed proprietary by the process developers.

PROCESS DESCRIPTION

UCC MGU. The UCC system is a batch process capable of processing up to 68 kg (150 lb) of coal per batch, over a 5-h duration, at temperatures of up to 816°C (1500°F) under atmospheric pressure to mild vacuum. Two 0.2-m- (8-in.-) diam. stainless steel tubes, each connected to 0.2 x 2.4 m (0.7 x 8 ft) tall sweep gas heaters located adjacent to the individual reactor tubes comprise the reactor system. Coal is fed to the reactor at the top, and the resulting char is withdrawn at the bottom. The liquids are condensed from the reactor effluent gas. Noncondensable gas is either recycled as sweep gas or flared (Chu, 1988).

Tests have been conducted on 38 mm x 0 (1.5 in. x 0) and 3 mm x 0 (1/8 in. x 0) Kentucky HK bituminous coal containing 33.8 wt % volatile matter, 59.4% fixed carbon, 5.0% ash, and 1.8% moisture. Ultimate analysis of the coal is C - 78.18%, H - 5.24%, N - 1.46%, S - 0.98%, Cl - 0.13%, and O - 9.01%. The optimum reactor temperature is considered to be 538°C (1000°F) for the best liquid quality. A small amount of sweep gas is maintained through the reactors to enhance the heatup rate (1.4 -18°C/min) and to reduce the residence time of the product gas in the reactor. Liquid yield on "as-received" coal is 12 to 15%, of which 4% is water.

KILnGAS Commercial Module (KCM). This is a 600-ton/d coal gasification demonstration plant which uses a ported, pressurized, rotary kiln gasifier. Coal entering the feed end of the gasifier is progressively dried and heated by hot producer gas as it moves toward the discharge end. The hot coal is devolatilized and then reacted with air and steam. Gasification occurs about midway through the gasifier and continues to the discharge end. Agglomerated ash is removed at the discharge end. Gasification occurs at 1037°C (1900°F) at 3.1 bar (45 psi) pressure. Devolatilization occurs around 537°C (1000°F).

The gasifier, which measures 3.2 x 41 m (10 x 136 ft), is divided into five zones with multiple air/steam ports in each zone.

The KILnGAS process can gasify a wide variety of coals without requiring pretreatment. Most of the tests, however, have been done on high-sulfur Illinois No. 6 coal. Condensable hydrocarbons and tars are separated from the reactor effluent gas. The tar is recycled to the gasifier, and the condensates are processed in the wastewater pretreatment plant where the oils are recovered (Parekh, 1982).

SGI Pilot Plant. The SGI system is a small, batch-fed atmospheric pyrolyzer with a nominal operating temperature of 537°C (1000°F) and a residence time of 20 min, and is capable of feeding 22.7 kg (50 lb) of coal per batch. The coal tested is a Montana Rosebud subbituminous coal containing 39.0 weight % volatile matter, 51.8% fixed carbon, 19.8% moisture, and 5.0% ash. Ultimate analysis of this coal is C - 54.8%, H - 3.7%, N - 0.8%, S - 0.6%, and Cl - 0.02%. Liquid yield (naphtha and distillates) is 11 to 13% on a moisture-ash-free coal basis (Esztergar, 1987).

Coalite Commercial Plant. This is a commercial, low-temperature carbonization plant operating in the UK. Bituminous coal with a volatile content of 35% is carbonized in metal retorts at about 600°C (1112°F). The volatile products are condensed in water-cooled take-off pipes. The remaining noncondensable gases pass through electrostatic precipitators and are further condensed before they are recycled and used for heating the retorts. Liquid yield on an "as-received" coal basis is about 9% (W. A. Bristow, 1947).

CHARACTERIZATION METHODS AND RESULTS

The coal liquids were characterized by standard ASTM procedures in most cases; however, other well-accepted procedures were used for some parameters. The following properties were included in the characterization:

Elemental analysis (Leco analyzer)

Carbon

Hydrogen

Nitrogen \geq 1.0 wt %; (for N <1.0%, use modified Method 351.2, EPA

Methods for Chemical Analysis of Water and Waste)

Sulfur

Oxygen (by neutron activation)

- Water content (ASTM 96-73)
- Specific gravity (ASTM D 287-67)
- Viscosity (ASTM D 88)
- Heating value (ASTM D-2015-85)
- Simulated distillation curve by gas chromatography (ASTM D-2887)
- Aliphatics/Aromatics (Proton NMR)

Two liquid samples were provided by UCCRC and were designated as UCC-1 (parametric run) and UCC-2 (production run).

A summary of the data obtained on the four coal liquids is presented in Table 1. For illustration, the simulated distillation curve for the UCC-1 liquid is shown in Fig. 1.

The following trends can be observed in Table 1:

1. H/C ratios of the coal liquids are less than the corresponding ratio for diesel fuel. Some degree of upgrading and/or blending will be required to enhance the H/C ratio if these liquids are to be substituted for diesel fuel.
2. Except for the SGI liquid, the H/C ratios are slightly lower than those found for liquids produced in a batch reactor in a previous study (Graves and Fox, 1984) where the carbonization temperature was below 500°C.
3. The viscosity of coal liquid is much higher than that of diesel fuel.
4. Aromatic carbon contents for the coalite and UCCRC liquids are similar but much higher than the aromaticity of the diesel fuel. Increase in aromaticity with a concomitant decrease in H/C ratio is indicative of increasing aromatic ring condensation. A priori, increased hydrogen content leads to decreased aromaticity (White et al., 1987).
5. Aromaticity of the KILnGAS liquid is the highest of all the liquids, which is attributable to process conditions. Process conditions in the KILnGAS gasifier are much more severe compared with Coalite, UCCRC, and SGI. The higher pressure, temperature, and longer residence time in the reactor could cause thermal cracking for this product, indicative of greater aromatic ring condensation (product contained elevated amounts of naphthalene).
6. The SGI liquid measured the lowest aromatic carbon, even less than that of diesel fuel. The sample from Test 1003, is a second-stage liquid, which is perhaps a much lighter fraction compared with the raw liquid. The high hydrogen and low oxygen contents of this liquid are puzzling.

UPGRADING STUDIES

Hydrotreating is the conventional technology used in the petroleum industry for heteroatom removal and product upgrading. It has also been used for upgrading liquids derived from several different coal liquefaction and shale oil processes. In a previous DOE-sponsored program designed to study the upgrading of coal- and oil shale-derived liquids, fixed-bed hydrotreating at three different severity levels was used to produce gasoline, jet, and diesel fuels from SRC II, Exxon Donor Solvent, and H-coal liquids. Satisfactory fuels were obtained, although high hydrogen consumption was observed [1000 to 3000 SCF/bbl, depending on the severity level and the coal liquid (Guerin, 1986)]. It was found that the hydrotreating operation was very sensitive to asphaltene-like impurities in the feed liquid. In addition to reducing their detrimental effect on catalyst performance, the removal of these impurities enabled significant reduction (factors of 1.5- to 3-fold) in the size of the hydrotreater reactor for jet fuel production (Sullivan, 1981).

Hydrotreating, requiring high-pressure equipment, catalysts, and hydrogen, is expensive and difficult because of the nature of the coal liquids. Chemical means of upgrading have the potential to be more cost effective. Primary emphasis, in the upgrading studies reported in this work, was on the removal of the basic nitrogen fraction from these coal condensibles by solvent extraction with acidic reagents. Principal reagents tested included formic, acetic, and

phosphoric acids in concentrations ranging from 25 to 90 vol %. The effect of acid strength was briefly examined on an early UCCRC condensible using acetic (pKa = 4.75), monochloroacetic (pKa = 2.85), and trichloroacetic (pKa = 0.70) acids at 50 vol % concentrations.

Extraction Studies on UCCRC Liquids

Illustrated in Table 2 is a comparison of formic and acetic acid extractions at 50, 75, and 90 vol % (formic only) concentrations using one of the early samples of UCCRC coal condensibles. Early samples from the UCCRC MGU were obtained under nonoptimum operating conditions and at a higher operating temperature of about 1300°F (optimum temperature is now considered to be about 1000°F). This, of course, resulted in a somewhat more viscous and more highly aromatic liquid product having an H/C ratio of 0.88. Extraction data in Table 2 indicate better extraction by acetic acid, with 50.9% of the nitrogen removed by 75 vol % acetic acid. Oxygen assays show little tendency for the organic phase to retain water for extraction with either of these two acids. Qualitatively, acetic acid also showed better extraction of the basic nitrogenous fraction than either monochloroacetic or trichloroacetic acids, suggesting that increased acid strength did not improve nitrogen removal.

Phosphoric acid was tested as a nitrogen extractant during the course of this work, based on similar experiments on shale oil (Johnson, 1981). Acid concentrations of 25, 50, and 75 vol % were tested, utilizing the same UCCRC condensible liquid and contacting procedure employed with acetic and formic acids. Unextracted nitrogen assays were 0.46, 0.44, and 0.37 wt %, respectively, with the highest acid concentration providing the greatest removal (66%). A third phase, which made clean separations difficult to achieve, was formed for the higher concentrations (50 and 75 vol %) in these experiments. Note, however, that even at 25 vol % phosphoric acid concentration, the nitrogen removal was 57.4%, which is still better than that obtained with 75 vol % acetic acid extraction (50.9%).

A more representative sample of the UCCRC coal condensible liquid is UCC-1 in Table 1. Extractions of the nitrogen content of this product were attempted with both acetic and phosphoric acids. However, extraction with 75 vol % acetic acid proved impossible because, at this concentration, the two liquids were completely miscible. This suggests that the UCC-1 liquid is different from the previous liquids tested. The acetic acid concentration was reduced to 50 vol %, and nitrogen removal was compared to that obtained with 25 vol % phosphoric acid. Nitrogen content was reduced to 0.36 and 0.34 wt %, respectively, or 36% removal with acetic acid and 39% removal with phosphoric acid. Nitrogen removal was less complete for this liquid compared with the previous UCCRC samples, suggesting that the liquid generated at the lower gasifier temperature had a lower basic nitrogen content.

Extraction Studies on a KILnGAS Condensible

A relatively large sample (about 5 gal) of a KILnGAS condensible, described as a "high-naphthalene-content" product, was received through the courtesy of the Allis-Chalmers Coal Gas Corporation. Its elevated aromatic content was verified by the NMR analysis shown in Table 1. A vacuum distillation of this product was performed, and the fraction boiling under 650°F was collected. The nitrogen content was reduced by about 53% (to 0.31 wt %), and the H/C ratio was increased to 0.83. Little change was noted for the other heteroatoms. Extractions were performed on both the raw liquid and the distillate with varying concentrations of acetic acid. The results, shown in Table 3, indicate 67% reduction in nitrogen content for extraction of the raw product with 75 vol % acetic acid and 58% reduction for the distillate.

Extraction Studies on an SGI Liquid

The condensible product from SGI International was described as a second-stage product using coal from the Rosebud Mine in Montana. Few details are known about this particular sample; however, its appearance and analysis (see Table 1) suggested that, at the very least, it was some sort of distillate. Its analytical properties, with the exception of the nitrogen assay, were better than the typical commercial diesel fuel shown in Table 1. The aromatic content, as measured by NMR, and the oxygen and sulfur assays were unusually low for a coal condensible liquid.

Solvent extraction studies with both acetic and formic acids showed nearly complete removal of nitrogen (98 to 99%) at all concentrations tested (see Table 4). Clean separations were observed with this extremely light organic liquid, as indicated by the oxygen assays of the organic phase. The nitrogen removal demonstrated for this product, coupled with the already low oxygen, sulfur, and aromatic assays, is probably sufficient to enable it to be used directly as a fuel in some diesel engines; however, its actual relationship to a working mild gasification process remains to be verified.

CONCLUSIONS

The characterizations of the condensible products from various coal gasification projects give an indication of the need for upgrading in order to produce a fuel suitable for transportation uses. It is evident that lower temperatures (<1000°F) in the gasifier are desirable in order to reduce aromatic content and subsequently increase the H/C ratios.

Solvent extraction studies on limited amounts of three condensible liquids must be deemed tentative. However, based only on raw material prices (acetic acid -- \$0.27/lb; formic acid -- \$0.365/lb; and phosphoric acid, 85% -- \$0.255/lb), the most economical process would utilize 25 vol % phosphoric acid as an extractant. Extraction experiments performed with several condensible samples showed that 75% recovery of the nitrogen-depleted organic phase was achievable with careful attention to experimental procedure. However, it should be pointed out that the aqueous raffinate from any solvent extraction process of this nature may generate an environmental disposal problem that has not been addressed during the course of this work.

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Table 1. Summary of coal liquids characterization data

Properties	Coalite	UCC-1 (parametric run)	UCC-2 (production run)	Kilm- GAS	SGI	Typical commercial diesel fuel
Elemental analysis (wt %)						
C	80.83	84.24	83.69	88.45	87.34	86.5
H	8.57	9.42	9.34	5.58	12.96	12.8
S	0.72	0.42	0.39	4.6	0.07	0.3
N	1.02	0.56	0.68	0.66	0.40	0.01
O (by neutron activation)	7.74	4.89	5.11	1.6	0.171	
H/C	1.27	1.34	1.34	0.76	1.77	1.78
Water content, %	1.80	0.790	0.900	0.14	0.004	nil
Specific gravity (at 25°C)	1.03	0.972	0.989	1.133	0.872	0.85
Viscosity (at 25°C), CP	290.0 ^a	12.06 ^b	25.55 ^b	34.0 ^b	18.0 ^b	3.0 ^b
Heating value, Btu/lb	16,300	17,100	17,000	16,500	19,400	18,150
Aromatic hydrogen content, wt %	30.4	30.2	26.9	86.1	8.7	14-16
Aromatic carbon content, wt %	57.7	55.9	52.4	94.8	20.0	34-37
Aliphatic hydrogen content, wt %	61.8	59.2	68.1	13.9	91.3	84.0
Simulated distillation data						
Initial BP, °C	147	48	58	58	142	
Final BP, °C	437	397	425	431	433	
Average BP, °C	234	214	211	218	273	
Percentage of oil distilled at 246°C	56	67	75	66	34	

^aMeasured by a Brookfield viscometer.^bMeasured by a Canon-Fenske viscometer.

ASTM average temperature corresponding to the 50% boiling point for diesel fuel.

Table 2. Extraction studies on a UCCRC liquid with aqueous formic and acetic acids

Element	Raw liquid	Organic-phase concentration, wt %					
		Formic acid			Acetic acid		
		50 ^a	75 ^a	90 ^a	50 ^a	75 ^a	90 ^a
Nitrogen	1.08	0.85	0.74	0.59	0.56	0.53	b
Oxygen	5.24	4.70	4.64	7.96	4.54	4.79	b

^aVol %.

^bInsufficient sample for analysis.

Table 3. Extraction of nitrogen from raw and distilled KILnGAS products using acetic acid

Acetic acid (vol %)	Remaining nitrogen, wt %	
	Raw KILnGAS ^a	<650°F distillate ^b
25	0.31	0.22
50	0.32	0.17
75	0.22	0.13
90	0.21	NA ^c

^aOriginal N content, 0.66 wt %.

^bOriginal N content, 0.31 wt %.

^cNot analyzed.

Table 4. Extraction studies on an SGI liquid with aqueous formic and acetic acids

Element	Raw SGI	Organic-phase concentration, wt %							
		Formic acid				Acetic acid			
		25 ^a	50 ^a	75 ^a	90 ^a	25 ^a	50 ^a	75 ^a	90 ^a
Nitrogen	0.40	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	0.02	<0.01
Oxygen	0.16	0.12	0.13	0.11	0.10	0.14	0.11	0.10	0.08

^aVol %.

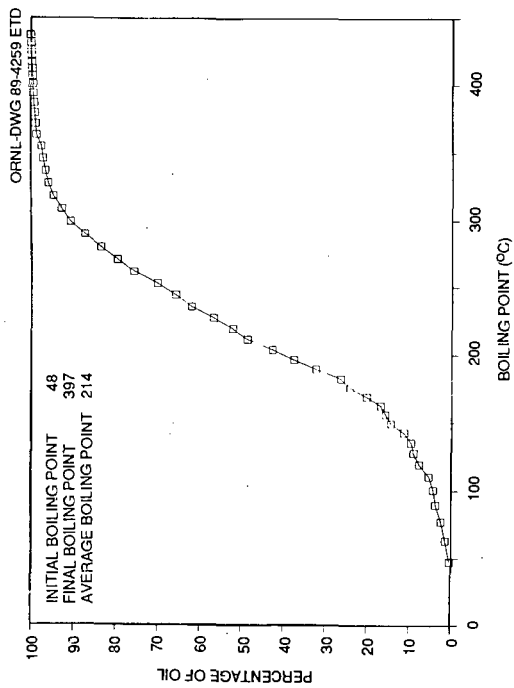


Fig. 1. Simulated distillation curve for UCC-1 coal liquid.